

Prediction of absorption spectra: Exploration of TDDFT and PCM on conjugated chains

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Purpose

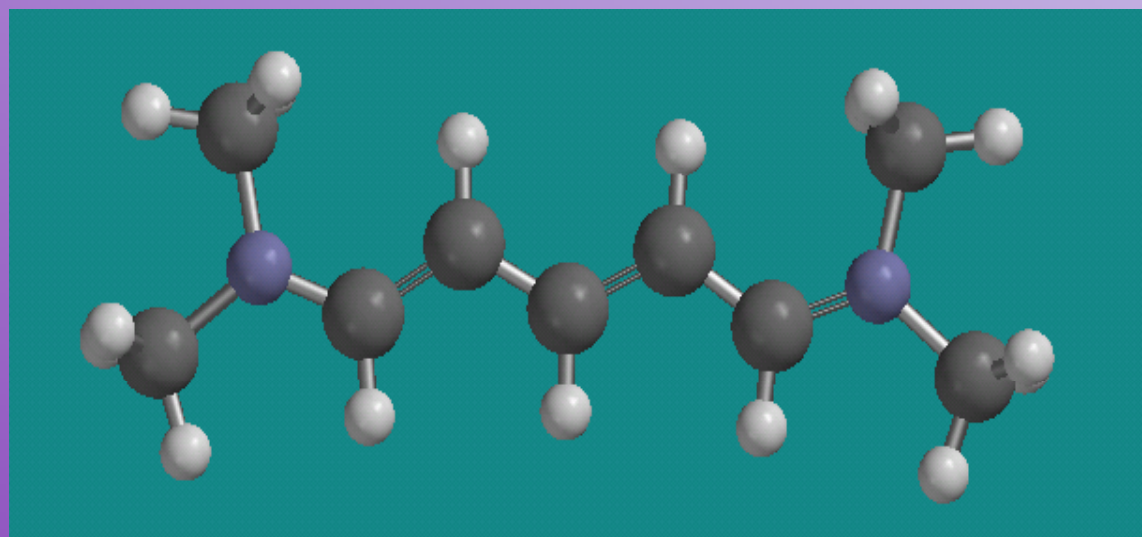
- A streptocyanine dye monomer was used to synthesize two unique dimers in a previous experimental study.¹
- Dimers demonstrated unexpected spectra in the UV-vis range.
- Our ultimate goal: Use quantum chemistry methods to accurately predict the excited states and absorption spectra of the dimer molecules.

Defining terms

- TDDFT – Time Dependent Density Functional Theory
 - Relatively newer method for computationally predicting excited electronic states
- PCM – Polarized Continuum Model
 - Models the solvent interacting with the solute in equilibrium
 - PCM has been shown to be a reliable method in other studies comparing experimental data to computational results²⁻⁴

Monomer

5-dimethylaminopenta-2,4-dienylenedimethylammonium chloride



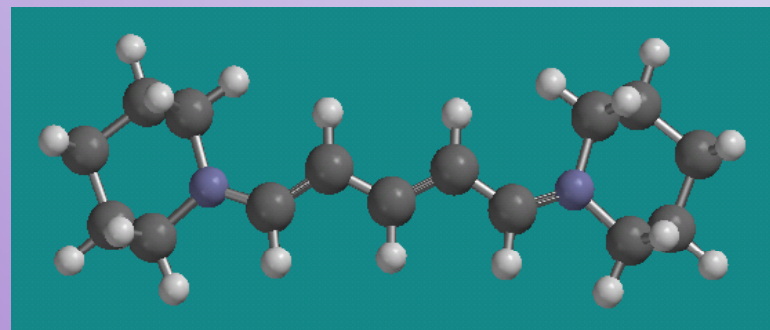
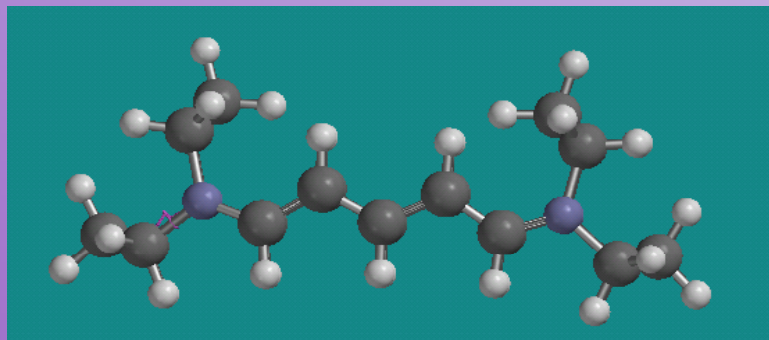
Take note of the alternating double bonds that exist between the two nitrogen atoms.

Dimers

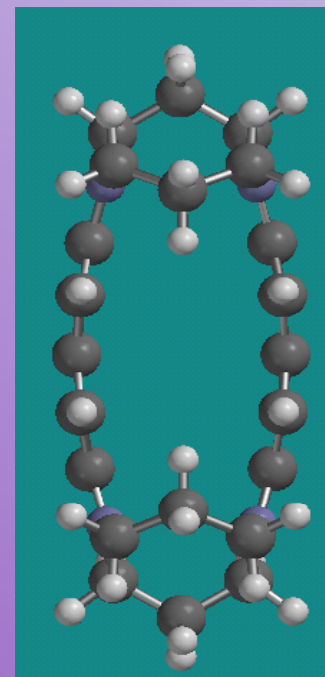
Dimer 1

Dimer 2

Side view



Top view



Plan of action

1. Find a suitable computational method to predict excited states of these molecules.
2. Calculate excited states for straight-chain alkenes while examining solvation effects.
3. Use data from alkene calculations to compare with experimental literature values.
4. Follow a linear scaling procedure⁵ using these comparisons to adjust for error in calculating streptocyanine monomer and dimers

Computational resources

- Calculations were performed on the MU3C cluster located at Hope College
 - Gaussian 09 was used for all TDDFT calculations
 - WebMO was occasionally used to build molecules and run calculations
- Pictures of molecules modeled in this presentation were created using Spartan '10 on a local machine

Choosing a computational method

- Excited State Calculations
 - TDDFT: Past studies had shown it to be agreeable with experimental results^{2,6-8}
 - 6-311+G* basis set was used: Diffuse functions on non-H atoms yielded greater accuracy with TDDFT²
 - Polarization and diffuse functions on hydrogens were found not to have a great impact on accuracy⁷
 - Test exchange-correlation functionals with a relatively high percentage of HF exchange⁶
 - High HF percentage helps to avoid self-interaction error common in TDDFT⁹⁻¹¹

Choosing a functional

- Calculated excited state transitions for 1,3-butadiene
- Tested functionals were chosen based on a previous comprehensive study;⁶ we chose four of these for testing on our system

Functional	State 1 transition (nm)	State 1 transition (eV)	Difference from Lit value (eV)	Approx calculation cpu time (min)
B3LYP	212.91	5.8233	-0.1133	28
BMK	212.48	5.8351	-0.1251	63
M062X	214.45	5.7815	-0.0715	52
ω B97X	211.09	5.8735	-0.1635	85

- Experimental literature value¹² for butadiene was 217 nm (5.71 eV)
- M062X fit literature value the closest and was relatively cheap

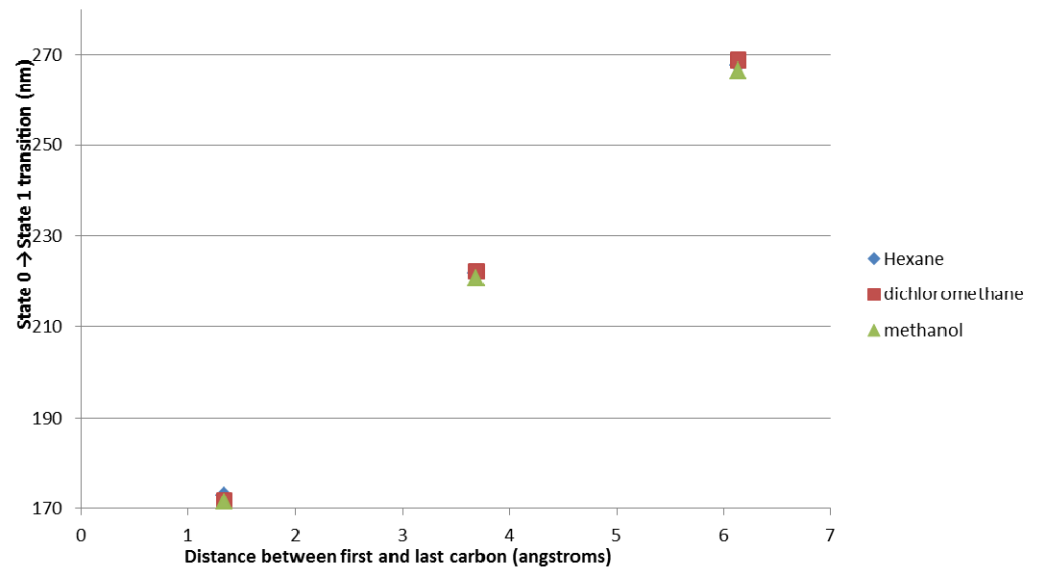
Excited state transitions

- First three excited state transitions were calculated for ethene, 1,3-butadiene, and 1,3,5-hexatriene.
 - These molecules were used to emulate the conjugated double bonds found in the monomer/dimers
- PCM used for solvation calculations
 - Methanol and dichloromethane were the experimental solvents used for the dye systems
 - Hexane is the solvent used in the literature values for the alkenes

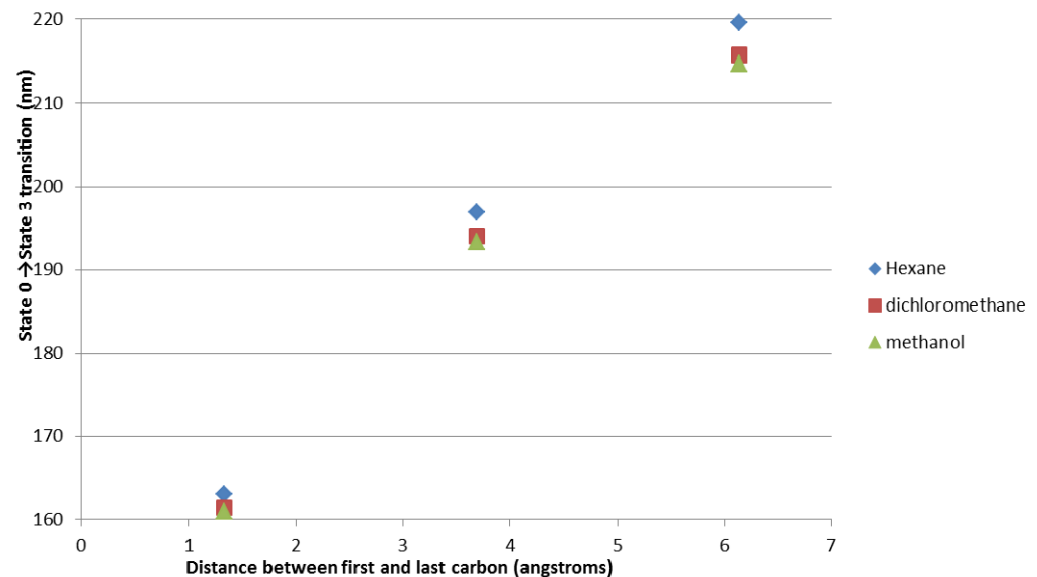
Alkenes in solvent

- Graphs of the first and third transitions
- Solvent effects have a greater impact in the third transition than the first.

Alkenes ethene, butadiene, and hexatriene in 3 different solvents

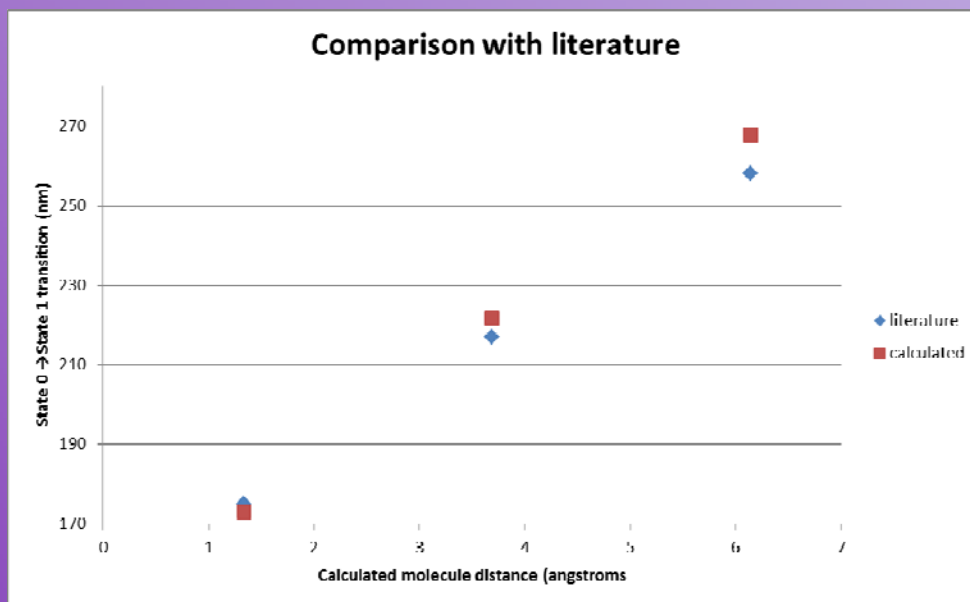


Alkenes ethene, butadiene, and hexatriene in 3 different solvents



Calculations vs. literature

- Ethene, 1,3-butadiene, and 1,3,5-hexatriene in hexane compared to experimental literature values in hexane
- The overestimation of the wavelength of transition became greater as the size of the molecule increased

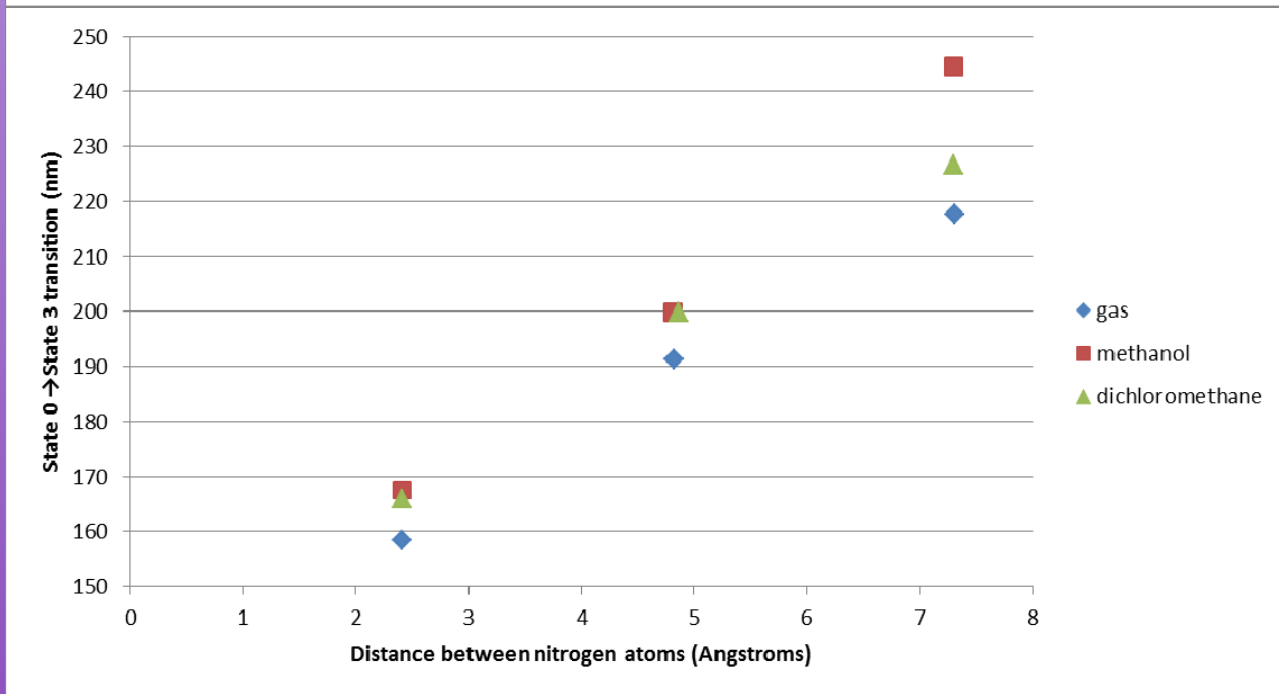
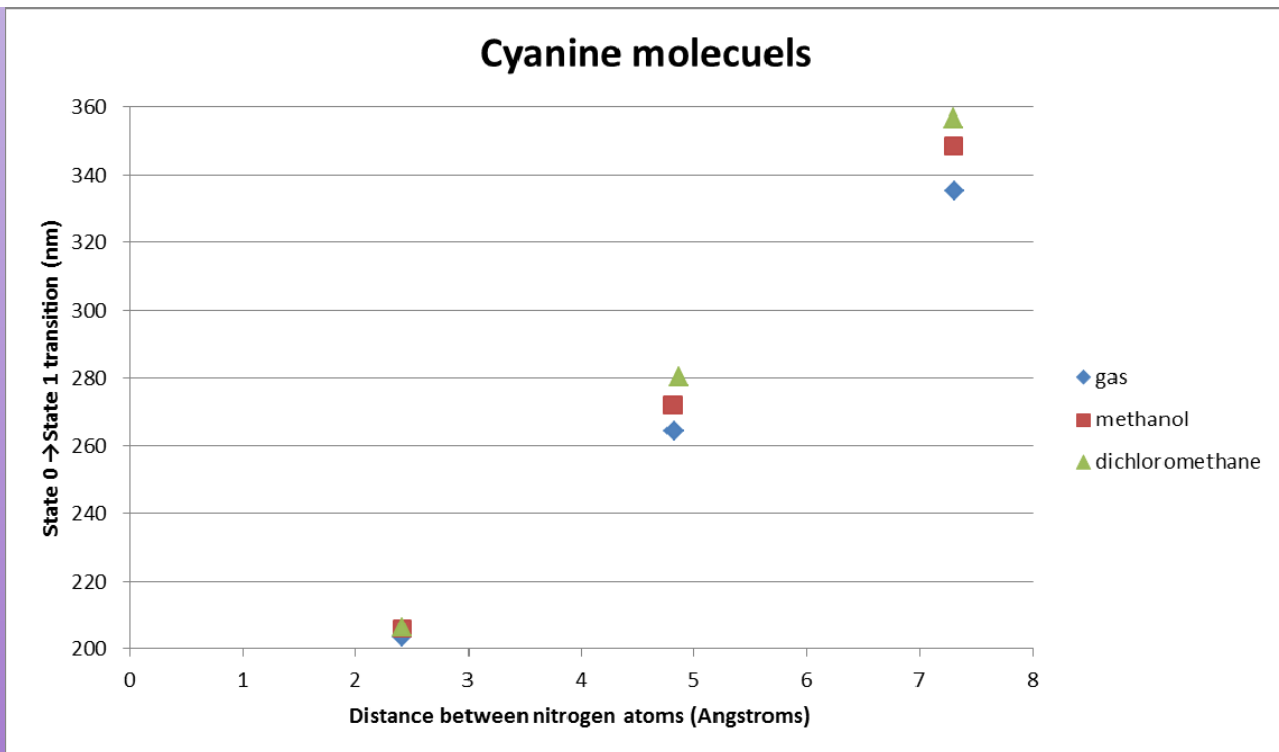


Streptocyanine monomer

- Calculations were performed on the cyanine monomer and two variations of the monomer that had one and three carbons connecting the nitrogen atoms instead of five
- Results of these calculations are on the next slide.

Monomer excited state calculations

- Solvent effects are larger for the third excited state transition.



Monomer excited state calculations cont.

- Overall trends are similar to those observed in the alkene calculations
- In all cases, gas phase calculated a shorter transition wavelength than those in solution
- For the monomer (longest of the cyanine molecules calculated), the large difference in wavelength for dichloromethane and methanol in the transition to the third excited state was unexpected

Conclusions and future work

- All studies involve quantum chemical calculations of excited states
- Functional study: M062X was found to be accurate without being too costly.
- Alkenes: solvent study and comparison to experimental literature showed consistent trends
- Streptocyanine monomers of similar lengths as alkenes: gas phase and solvent study gave similar trends as the alkenes
- Planned: Full calculations of excited states in dimers will be adjusted for error and then compared with experimental spectra

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End

